Apparent First-Order Wetting and Anomalous Scaling in the Two-Dimensional Ising Model

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The global phase diagram of wetting in the two-dimensional Ising model is obtained through the exact calculation of the surface excess free energy. In addition to a surface field for inducing wetting, a surface-coupling enhancement is also included. The wetting transition (of second order) is critical for any finite ratio of surface coupling J_s to bulk coupling J, and becomes of first order in the limit $J_s/J \to \infty$. However, for $J_s/J \gg 1$, the critical region is exponentially small and is practically invisible to numerical studies. A distinct preasymptotic regime exists in which the transition displays first-order character. In this regime, surprisingly, the surface susceptibility and surface specific heat develop a divergence and show anomalous scaling with an exponent equal to $3/2$.

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When a surface is exposed to an adsorbate at two-phase coexistence, either droplets (partial wetting, or "nonwet") or a uniform layer (complete wetting, or "wet") of one of the phases may form on it. Delicate tuning of surface or bulk properties may allow one to achieve a surface phase transition or critical phenomenon from partial to complete wetting. The so-called wetting transition has been studied experimentally and theoretically for some 35 years now; for reviews, see, e.g., [1–5]. The first exact solution beyond mean-field theory revealed a critical wetting transition (of second order) in the 2D Ising model with a surface field [6,7]. When antiferromagnetic surface couplings are added, critical wetting persists [8]. However, for strong ferromagnetic surface couplings, new physics arises, as we show in this Letter.

Monte Carlo simulations of wetting in the 3D Ising model with a surface field *and* a surface-coupling enhancement have unveiled a rich global phase diagram, featuring first-order and critical wetting separated by tricritical wetting [9], in accord with qualitative predictions from Landau theory [10]. However, in two dimensions ($d = 2$), where thermal fluctuation effects on wetting are pronounced, only critical wetting transitions belonging to a single universality class are expected [2,11,12]. Nevertheless, an exact calculation revealed that first-order wetting is possible when an extra defect line is introduced [13]. Furthermore, numerical evidence for first-order wetting was found in Monte Carlo simulations of the 2D Ising model with an extra spin state (a vacancy) [14–16].

We investigate the global phase diagram for wetting in $d = 2$ for short-range forces and answer the following fundamental questions. Is first-order wetting possible in $d = 2$ for the standard spin-$1/2$ Ising model with a surface, by enhancing the spin-spin coupling at the surface? What is the precise character of the wetting transition in $d = 2$; in particular, how wide is the critical region and are there distinct preasymptotic regimes?

Consider a set of Ising spins $\sigma(n,m) = \pm 1$ located at points (n,m) of the planar square lattice $\Lambda(n,m)$ such that $1 \le n \le N$, $1 \le m \le M$. The energy of a configuration $\{\sigma\}$ of spins is given by

$$\begin{aligned} E(\{\sigma\}) = &-\sum_{m=1}^{M}\{H_1(m)\sigma(1,m) + H_N(m)\sigma(N,m)\} \\ &-\sum_{m=1}^{M} J_0\sigma(1,m)\sigma(2,m) - \sum_{m=1}^{M} J_s\sigma(2,m)\sigma(2,m+1) \\ &-\sum_{m=1}^{M}\sum_{n=2}^{N-1} J_1\sigma(n,m)\sigma(n+1,m) \\ &-\sum_{m=1}^{M}\sum_{n=3}^{N-1} J_2\sigma(n,m)\sigma(n,m+1). \end{aligned} \tag{1}$$

The fields $H_1(m)$ and $H_N(m)$ allow us to fix boundary spins. The spin-spin coupling J_0 (> 0) acts as an effective surface field on the first layer ($n = 2$) of free spins; this is the usual wetting term, which for mixtures corresponds to a differential surface fugacity. We denote by $h_1 \equiv \beta J_0$ the absolute value of the (reduced) surface field, where $\beta = 1/k_B T$, with k_B the Boltzmann constant and T the absolute temperature. Modified spin-spin couplings J_s along the surface take into account the changed environment of molecular interactions at the surface in such a way that exact solution is still possible. J_1 and J_2 are the usual (ferromagnetic) "bulk" nearest-neighbor couplings. Periodic boundary conditions $\sigma(n, M+1) = \sigma(n, 1)$, which we impose, are essential to generate exact solutions.

The normalized canonical probability is $P(\{\sigma\}) = Z^{-1}\exp[-\beta E]$, where Z is the partition function.

We will make use of two types of "wall" boundary conditions, as follows:

$$A\colon\ H_1(m), H_N(m) = +\infty, \quad \text{for } 1 \le m \le M, \tag{2}$$

which, for $T \le T_c$, with T_c the bulk critical temperature, force a state with positive spontaneous bulk magnetization in the thermodynamic limit $M \to \infty$ followed by $N \to \infty$, and

$$B\colon H_1(m) = \begin{cases} -\infty, & \text{for } 1 \le m \le S \\ +\infty, & \text{for } S < m \le M, \end{cases}$$
$$H_N(m) = +\infty, \quad \text{for } 1 \le m \le M, \tag{3}$$

which force a long contour of surface length S, beginning at $(1, \frac{1}{2})$ and ending at $(1, S + \frac{1}{2})$, which delimits the region of predominantly negative magnetization.

The surface excess free energy f (per unit length of surface, S) can be obtained from

$$\beta f = -\lim_{S\to\infty}\lim_{\Lambda\to\infty}\frac{1}{S}\ln\frac{Z_B}{Z_A}, \tag{4}$$

where partition functions Z_A and Z_B correspond to the respective boundary conditions. In the language of wetting phenomena, this definition ensures that f equals $\gamma_{+-}\cos\theta_Y$ in the nonwet state and γ_{+-} in the wet state ($\theta_Y = 0$), where θ_Y is Young's contact angle and γ_{+-} is the surface tension of a free interface between + and − phases in bulk. We obtain the analytic form

$$\frac{Z_B}{Z_A} = \frac{i}{2\pi}\int_0^{2\pi} d\omega e^{iS\omega}\tan\delta^*(\omega/2)\frac{(e^{\gamma(\omega)} - Q_+)(e^{\gamma(\omega)} - Q_-)}{(e^{\gamma(\omega)} - P_+)(e^{\gamma(\omega)} - P_-)}, \tag{5}$$

where $\gamma(\omega)$, $\delta^*(\omega)$ are elements of the Onsager hyperbolic triangle,

$$\cosh\gamma(\omega) = \cosh 2K_1^*\cosh 2K_2 - 2\sinh 2K_1^*\sinh K_2\cos\omega \tag{6}$$

and

$$\cosh 2K_1^* = \cosh 2K_2\cosh\gamma(\omega) - \sinh K_2\sinh\gamma(\omega)\cos\delta^*(\omega), \tag{7}$$

with $K_i \equiv \beta J_i$, and with dual couplings K_i^* satisfying $\tanh K_i^* = e^{-2K_i}$ for $i = 1, 2$. The quantities $P_\pm$ and $Q_\pm$ are real valued and independent of ω.

The integrand is singular at values of ω for which $e^{\gamma(\omega)} = P_\pm$. The results for $P_\pm$ are

$$P_\pm = \frac{s \pm \sqrt{s^2 - r^2 + 1}}{r + 1}, \tag{8}$$

where, defining $2K_2' \equiv 4K_s - 2K_2$ with $K_s \equiv \beta J_s$,

$$r = \frac{e^{2K_2'} - \cosh 2K_2}{\sinh 2K_2} \tag{9}$$

and

$$s = \cosh 2K_1^*\frac{e^{2K_2'}\cosh 2K_2 - 1}{\sinh 2K_2} - e^{2K_2'}\sinh 2K_1^*\cosh 2h_1. \tag{10}$$

The $Q_\pm$ have similar structure to the $P_\pm$ but, crucially, never coincide with the $P_\pm$. Hence, they cannot remove the simple poles coming from the zeros in the denominator of (5), needed to establish the limiting free energy. The details of $Q_\pm$ do not contribute to the location of the poles but only to the residues, and will be given elsewhere.

Henceforth we assume isotropy in bulk, $J_1 = J_2 = J$, so $K_1 = K_2 = K$. The singularity is given by $P_+ = 1$; for $P_+ > 1$ (the nonwet state), f is obtained through

$$\cosh\beta f = \cosh(2K - 2K^*) + 1 - \frac{1}{2}\left(P_+ + \frac{1}{P_+}\right), \tag{11}$$

while for $P_+ < 1$ or complex P_+ (the wet state), $\beta f = 2K + \ln\tanh K$, which equals $\beta\gamma_{+-}$ [17,18].

For a given K we denote the value of h_1 at wetting by h_{1w}. For the special case $J_s = J$ (which was solved in 1980), the critical wetting phase boundary satisfies $e^{2K}(\cosh 2K - \cosh 2h_{1w}) = \sinh 2K$ [6,7]. Figure 1 shows critical wetting phase boundaries for $J_s \ge J$. For $J_s/J = \infty$ we obtain $\cosh^2 2K/\sinh 2K - \cosh 2h_{1w} = 1$, which simplifies to

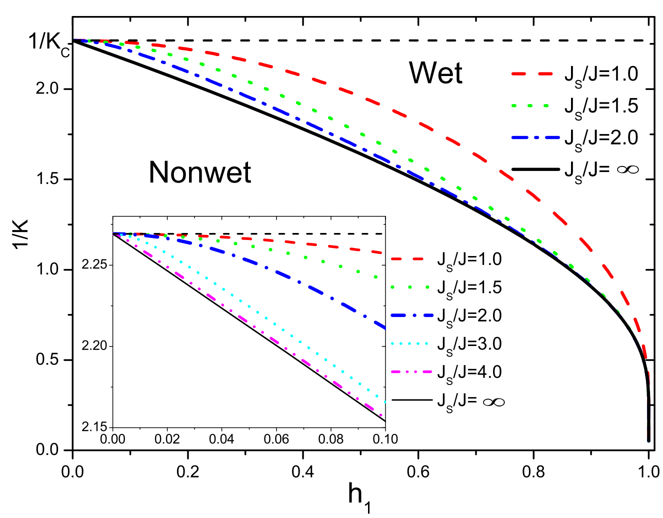

FIG. 1. Wetting phase boundaries in surface field h_1 and temperature $1/K$, for various surface-coupling enhancements J_s/J. For finite J_s/J the wetting transition is of second order and the phase boundary is parabolic near $h_1 = 0$, whereas for $J_s/J = \infty$ the wetting transition is of first order and the phase boundary is linear near $h_1 = 0$. The horizontal dashed line marks bulk criticality.

$$h_{1w} = K - K^* = K + \frac{1}{2}\ln\tanh K, \quad \text{for } J_s/J = \infty, \tag{12}$$

and has a simple physical interpretation. For $J_s/J \gg 1$ (the surface ferromagnetic limit) the surface magnetization $\hat{m}_1$ (at $n = 2$ on the lattice) saturates to $+1$ or -1, since all surface spins are aligned. The wetting transition is induced by a massive surface spin flip from -1 to $+1$, causing an interface between $+$ and $-$ phases in bulk to unbind from the surface. Anticipating a first-order transition for $J_s/J \to \infty$, we can conjecture h_{1w} simply by equating the surface energy gain of wetting to the surface tension cost of a free interface.

The phase boundary for $J_s/J = \infty$ is linear near the bulk critical point. For $K \to K_c$, $h_{1w} \sim 2(1 - K_c/K)$, where $K_c = \frac{1}{2}\ln(1 + \sqrt{2}) \approx 0.4407$ is the bulk critical coupling. This differs from the quadratic (or higher-order) behavior found for the critical wetting phase boundary near bulk T_c for finite J_s/J. The linear character is reminiscent of mean-field first-order wetting near surface-bulk multicriticality, with tricritical wetting for $T \to T_c$ [10].

Remarkably, the wetting transition already appears to be of first order at large but finite J_s/J. Figure 2 shows the surface excess free energy f near the transition. We fix the temperature through $1/K = 2$ and vary h_1. In Fig. 2(a), a sharp corner clearly appears for $J_s/J = 6$, suggesting first-order behavior. The singular part of f is shown in Fig. 2(b). We denote the value of f at wetting by $f_w \equiv f(h_{1w})$. The simple behavior $f_w - f \propto (h_{1w} - h_1)^2$ found for $J_s/J = 1$ is the signature of second-order wetting. However, for larger surface coupling, say $J_s/J > 4$, there is an extended range of h_1 for which $f_w - f \propto (h_{1w} - h_1)$, which indicates first-order character. Only very near the transition does $f_w - f$ cross over from $(h_{1w} - h_1)$- to $(h_{1w} - h_1)^2$-like behavior. In the regime where $f_w - f \propto (h_{1w} - h_1)$, the transition is effectively of first order.

The emerging first-order character is conspicuous in the surface excess magnetization m_1, defined as $m_1 \equiv -\beta(\partial f/\partial h_1)$ and related to the surface magnetization $\hat{m}_1$ through $m_1 = \hat{m}_1 + 1$, so that $m_1 = 0$ in the wet state. Figure 3 shows m_1 for $1/K = 2$. In Fig. 3(a), m_1 develops a steplike singularity as J_s/J is increased. Figure 3(b) shows detail near the transition point. For large J_s/J, m_1 stays constant (at $m_1 = 2$) until very close to the transition, and eventually crosses over to the second-order transition behavior; this is a linear decrease $m_1 \propto (h_{1w} - h_1)$, which corresponds to lines of slope 1 in Fig. 3(b).

New physics arises when examining the surface susceptibility and the surface specific heat. Accompanying the emerging first-order character, there is anomalous scaling in the surface susceptibility χ_{11}, defined as the second derivative of f with respect to h_1. Figure 4(a) shows χ_{11} for different J_s/J at $1/K = 2$. For the standard second-order wetting transition, χ_{11} makes a finite jump. For large J_s/J, the jump is still finite but very large. Near the transition point, χ_{11} displays an apparent divergence according to a power law as h_1 approaches h_{1w} from below (the nonwet state). For example, for $J_s/J = 6$, we find $\chi_{11} \propto (h_{1w} - h_1)^{-3/2}$ for $10^{-9} < h_{1w} - h_1 < 10^{-3}$, implying an effective exponent for χ_{11} equal to $3/2$. This cannot be explained by

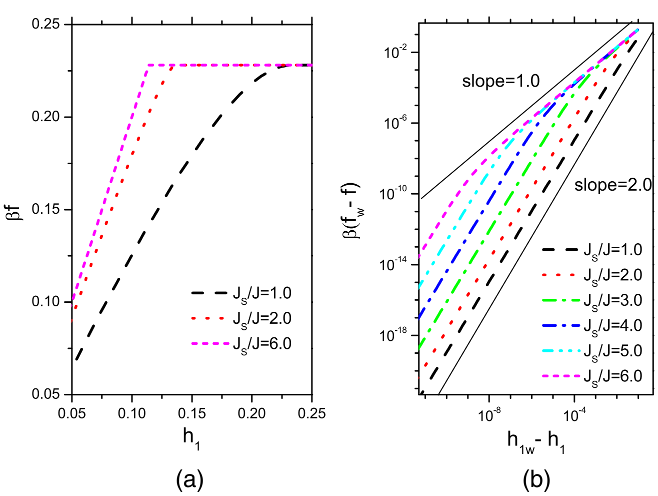

FIG. 2. Surface excess free energy f versus surface field h_1. (a) The transformation of a parabolic singularity (second-order transition) into a corner (apparent first-order transition) as J_s/J is increased. (b) The crossover from apparent first-order to asymptotic second-order character in the free-energy singularity, in a log-log plot. Solid lines with slopes 1 and 2 have been added (thin black lines). The temperature $T(< T_c)$ is fixed through $1/K = 2$.

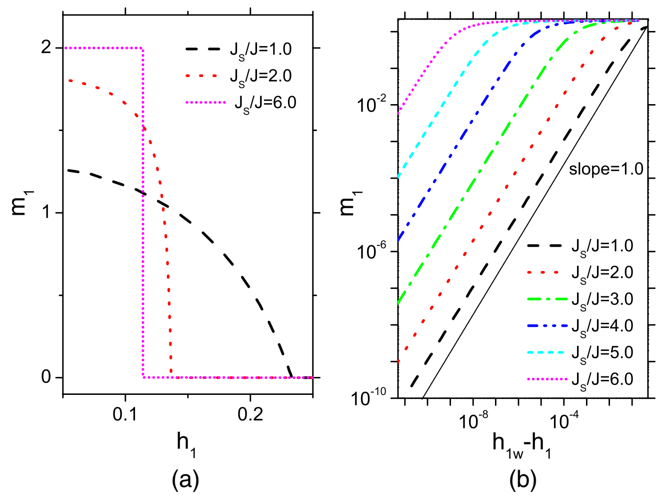

FIG. 3. Surface excess magnetization m_1 versus surface field h_1. (a) The linear approach to zero for (second-order) critical wetting gradually transforms into an apparent discontinuity as J_s/J is increased, indicating first-order character. (b) The crossover from first-order (piecewise constant) to second-order character (vanishing with critical exponent 1), in m_1 versus surface field in a log-log plot. A solid line with slope 1 has been added (thin black line).

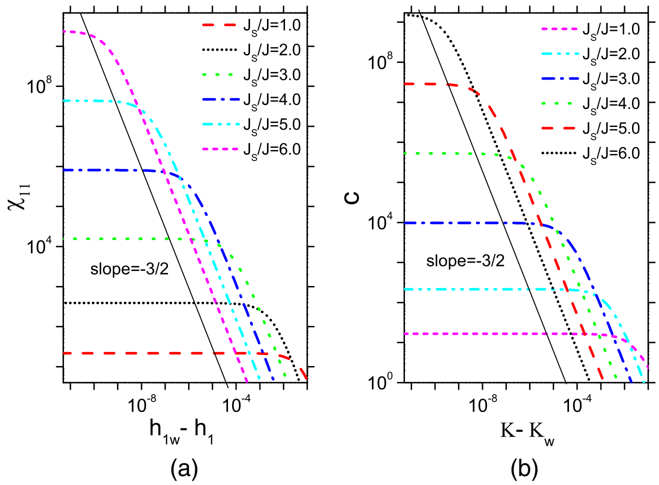

FIG. 4. Anomalous scaling of (a) the surface susceptibility χ_{11} and (b) the surface specific heat c. The apparent divergence, with exponent $3/2$, is manifest and persists until the critical region is reached. There, a crossover to a constant value takes effect. This value is the magnitude of the jump in the thermodynamic response function at critical wetting. Note how the critical region shrinks as J_s/J is increased [cf. Eq. (18)]. Solid lines with slope $-3/2$ have been added (thin black lines).

the usual scaling relations. A similar anomaly is found for the surface specific heat c, which is proportional to the second derivative of f with respect to $1/K$. Figure 4(b) shows c for different J_s/J, with h_1 fixed at the value of h_{1w} found for $1/K = 2$. The exponent characterizing the apparent divergence of c at wetting for large J_s/J also equals $3/2$.

We now demonstrate the robustness of the linear dependence of f on h_1 near the wetting transition for $J_s/J \gg 1$, and we explain the anomalous scaling. For $J_s/J \gg 1$, we have $K_2' \sim 2(J_s/J)K$, so in view of (9), $r \gg 1$. We fix K and vary h_1. At the transition, $r = s(h_{1w})$. We expand s about h_{1w}, with $1 \gg \Delta h_1 \equiv h_{1w} - h_1 > 0$,

$$s(h_{1w} - \Delta h_1) = r\{1 + 2\Delta h_1 \sinh 2h_{1w} + \mathcal{O}((\Delta h_1)^2) + \mathcal{O}(\Delta h_1/r)\}. \qquad (13)$$

The form (8) of P_+ suggests two important scaling limits. The first is the critical limit $r^2(s/r - 1) \ll 1$, to which we will return later. The second is the strong surface-coupling limit $r^2(s/r - 1) \gg 1$, or $1 \gg \Delta h_1 \gg e^{-8(J_s/J)K} = e^{-8K_s}$. In this limit, we obtain

$$P_+ = 1 + \sqrt{2\Delta h_1 \sinh 2h_{1w}} - 1/r + \mathcal{O}((\Delta h_1)^2) + \mathcal{O}(\Delta h_1/r) + \mathcal{O}(1/r^2). \qquad (14)$$

The free energy difference $f_w - f$ in this limit is interesting. Using (11), we obtain the surprising form

$$\beta(f_w - f) = 2\Delta h_1 - \frac{2}{r}\sqrt{\frac{\Delta h_1}{\sinh 2h_{1w}}} + \mathcal{O}((\Delta h_1)^2) + \mathcal{O}(\Delta h_1/r) + \mathcal{O}(1/r^2), \qquad (15)$$

implying that the transition is effectively of first order, since the second term is much smaller than the first due to the prefactor $1/r$. However, this nonlinear correction term becomes all important when taking the second derivative of the free energy. Thus, Eq. (15) allows one to instantly capture the anomalous scaling for the surface susceptibility,

$$\chi_{11} \propto (\Delta h_1)^{-3/2}. \qquad (16)$$

In the "temperature" direction, we can get similar but more complicated expansions. If we fix h_1 and J_s/J, and expand the free energy about the wetting point $K = K_w$, we obtain, with $\Delta K \equiv K - K_w > 0$,

$$\beta(f_w - f) \approx \frac{A}{2\sinh 2h_1}\Delta K - \frac{1}{2r\sinh 2h_1}\sqrt{2A\Delta K}, \qquad (17)$$

where $A \equiv \mathcal{A}(K_w, h_1, J_s/J) \equiv \partial \ln(s/r)/\partial K|_{K=K_w}$. This clarifies why there is also anomalous scaling in the specific heat, with the same exponent $3/2$, as illustrated in Fig. 4(b).

No matter how large J_s/J is, the asymptotic behavior in the limit $\Delta h_1 \to 0$ is invariably critical wetting (with a second-order transition). The only exception is $J_s/J = \infty$, for which (15) holds exactly with $1/r = 0$. The asymptotic behavior for all finite J_s/J is easily obtained in the critical scaling limit $r^2(s/r - 1) \ll 1$, with the result $f_w - f \propto (\Delta h_1)^2$. However, for large J_s/J the critical region is *exponentially small*, i.e.,

$$0 \le \Delta h_1 \ll e^{-8(J_s/J)K}. \qquad (18)$$

The global wetting phase diagram at bulk coexistence in the variables h_1 and J_s/J, featuring the surface ferromagnetic as well as antiferromagnetic regime, is presented in Fig. 5 for a representative fixed temperature $1/K = 2$. The phase boundary separating the wet and nonwet regions (solid line) consists of critical wetting but develops apparent first-order character for large J_s/J. True first-order wetting is obtained for $J_s/J = \infty$.

For $J_s < 0$ (antiferromagnetic surface coupling) and large $|J_s/J|$ the surface forms a perfect antiferromagnetic chain, and $\hat{m}_1 = 0$ unless the (uniform) surface field is strong enough to break the staggered surface order. Depinning becomes possible for $K_0 > -2J_s$ or $h_1 > -2(J_s/J)K$. This defines the slope of the asymptote for large $|J_s/J|$ to the critical wetting phase boundary found for $J_s < 0$.

The apparent first-order character of the wetting transition for large J_s/J can be interpreted physically. In the solid-on-solid model description of interface delocalization

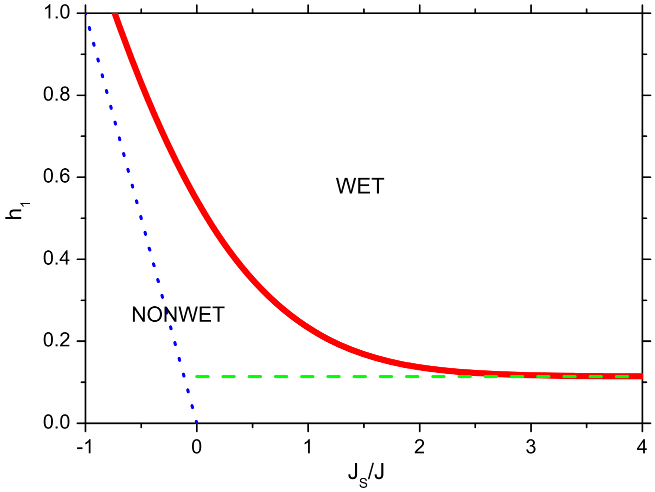

FIG. 5. Global wetting phase diagram at bulk coexistence in surface field h_1 and surface-coupling enhancement J_s/J, for $1/K = 2$. Wet and nonwet regions are separated by critical wetting (red solid line), which develops first-order character when approaching the would-be first-order wetting line $h_{1w} \simeq 0.114\,03$ derived in the large J_s/J limit (green dashed line). The thin dotted line (blue) is parallel to the asymptote to the critical wetting line in the strongly antiferromagnetic surface regime.

in $d = 2$, the interface unbinds from the surface in a continuous and gradual manner for $J_s/J \lesssim 1$, while for $J_s/J \gg 1$ it can unbind only via quantum tunneling through a high activation barrier [2,11]. This can explain an *effective* first-order wetting transition, which crosses over to a continuous one only extremely close to the transition.

At large J_s/J, the ultimate crossover to critical wetting cannot be detected by accurate numerical techniques for finite systems (e.g., such as those developed in [19,20]) and it is unrealistic to expect that it could be seen in Monte Carlo simulation or in an experiment in a (quasi-) 2D system. The effective first-order transition with novel scaling properties, which we have highlighted, is for all practical purposes the dominant wetting behavior.

In conclusion, we have shown by exact solution that the wetting transition in the 2D Ising model is critical for all finite J_s/J, but displays first-order character for large J_s/J. This apparent first-order behavior is accompanied by anomalous scaling of the surface susceptibility and the surface specific heat, featuring for both quantities an apparent divergence with an exponent $3/2$.

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